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1 **Crystal structure of Ni-sorbed synthetic vernadite: A powder X-ray diffraction study**

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12

13 Running title: Structure of Ni-sorbed vernadite

14

ABSTRACT

Vernadite is a nanocrystalline turbostratic phyllomanganate ubiquitous in the environment, which contains nickel in specific settings such as oceanic sediments. To improve our understanding of nickel uptake in this mineral, two series of synthetic analogs to vernadite (δ - MnO_2) were prepared with Ni/Mn atomic ratios ranging from 0.002 to 0.105 at pH 4 and from 0.002 to 0.177 at pH 7, and their structures characterised using X-ray diffraction (XRD). The δ - MnO_2 nano-crystals are essentially monolayers with coherent scattering domain sizes of ~ 10 Å perpendicular to the layer and of ~ 55 Å in the layer plane. The layers contain an effective proportion of $\sim 18\%$ vacant octahedral sites, regardless of the Ni content. At Ni/Mn ratios $< 1\%$, XRD has no sensitivity to Ni, and the layer charge deficit is apparently entirely balanced by interlayer Mn, Na, and protons. At higher Ni/Mn ratios, Ni occupies the same site as interlayer Mn above and/or below layer vacancies together with sites along the borders of the MnO_2 layers, but the layer charge is balanced differently at the two pH values. At pH 4, Ni uptake is accompanied by a decrease in structural Na and protons, whereas interlayer Mn remains strongly bound to the layers. At pH 7, interlayer Mn is less strongly bound and partly replaced by Ni. The results also suggest that the number of vacant layer sites and multivalent charge-compensating interlayer species are underestimated in the current structure models for δ - MnO_2 .

35 **Introduction**

36

37 The phyllomanganate vernadite, like its synthetic analog δ -MnO₂ (McMurdie, 1944), is a
38 nanosized and turbostratic variety of birnessite, that is a layered manganese oxide consisting
39 of randomly stacked layers composed of MnO₆ octahedra (Bricker, 1965; Giovanoli, 1980). In
40 the structure model presently available for δ -MnO₂ (Villalobos *et al.*, 2006), the nano-sized
41 layers contain only Mn⁴⁺ cations and vacant octahedral sites (6%), whose charge is
42 compensated for by interlayer Na⁺ (Na_{0.24}(H₂O)_{0.72}[Mn⁴⁺_{0.94}vac_{0.06}]O₂). Vernadite likely
43 forms, at least in part, from the biologically-mediated oxidation of Mn(II) (Tebo *et al.*, 2004).
44 For example, different strains of fungi and bacteria have been shown to produce vernadite-
45 like oxides (Mandernack *et al.*, 1995; Jurgensen *et al.*, 2004; Tebo *et al.*, 2004, 2005; Webb *et al.*,
46 2005; Miyata *et al.*, 2006; Villalobos *et al.*, 2006). Their high metal sorption capacities
47 result from the combination of small particle size, which induces a high number of border
48 sites, and of vacant layer sites, which create a locally strong charge deficit.

49 As a result of this reactivity, vernadite has a key influence on the mobility of metals in a
50 variety of environments. For example, Ni and other trace metals were reported to be
51 associated with vernadite-like minerals in oceanic and lake ferromanganese nodules and
52 crusts (Aplin and Cronan, 1985; Bogdanov *et al.*, 1995; Koschinsky and Halbach, 1995; Lei
53 and Boström, 1995; Exon *et al.*, 2002; Koschinsky and Hein, 2003; Bodei *et al.*, 2007;
54 Peacock and Sherman, 2007a; Manceau *et al.*, 2007a). Similarly, in manganese coatings
55 deposited on water-processing filtration sands nickel is essentially bound to vernadite
56 (Manceau *et al.*, 2007b). Understanding the reactivity of vernadite with nickel and the
57 stability of Ni-complexes requires gaining insights into the metal-mineral interactions
58 occurring at the atomic scale. The ability of usual diffraction methods, such as the Rietveld

method, is however impaired by the minute size and extreme stacking disorder of these compounds.

This article reports structure models for Ni-sorbed δ -MnO₂ using X-ray diffraction (XRD), and chemical data. The layer and interlayer crystal structure and the mean number of stacked layers were determined from the trial-and-error simulation of the hk scattering bands and of the $00l$ reflections (Drits and Tchoubar, 1990; Plançon, 2002). This modelling approach was applied previously on synthetic and natural phyllomanganates differing in chemical composition and density of structural defects (Chukhrov *et al.*, 1985; Lanson *et al.*, 2000, 2002a, 2002b, 2008; Gaillot *et al.*, 2003, 2005, 2007; Villalobos *et al.*, 2006). The validity of the structure models was assessed from the comparison with Ni K-edge extended X-ray absorption fine structure (EXAFS) data and from bond valence calculations. Finally, structural mechanisms for the sorption of Ni onto δ -MnO₂ crystals are proposed from the integration of all results.

Experimental methods

Synthesis of δ -MnO₂ and Ni sorption protocol

The sample preparation was described previously (Manceau *et al.*, 2007b). Briefly, suspensions of Na-rich δ -MnO₂ were prepared following the protocol of Villalobos *et al.* (2003), kept hydrated for several days, and then equilibrated at pH 4 or pH 7 and enriched afterwards in Ni at constant pH by the slow (0.4 mL/min) dropwise addition of a 5×10^{-4} mol/L Ni(NO₃)₂ solution. After 12 h of equilibration, the suspensions were filtered, rinsed with a few mL of deionized water, and freeze-dried. The samples are named as in the previous study (Table 1).

84 *Chemical analysis*

85 The mean oxidation degree of manganese was determined by potentiometric titration using
86 Mohr salt $[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)]$ and $\text{Na}_4\text{P}_2\text{O}_7$ (Lingane and Karplus, 1946; Vetter and Jaeger,
87 1966). Three measurements were made on each sample, and a reference was measured after
88 each sample to ensure the absence of bias due to titrant ageing. Total Mn, Ni and Na contents
89 were determined with a Perkin-Elmer Optima 3000 ICP-AES (Inductively Coupled Plasma –
90 Atomic Emission spectrometer) on aliquots of solutions prepared from ~5 mg powder
91 digested in ~15 mL NH_3OHCl (0.7 mol/L, pH 1.9) for 1 minute. Results are reported in
92 Table 1.

93
94 *X-ray diffraction*

95 Powder X-ray diffraction (XRD) patterns were recorded over the 5-80 °2 θ angular range
96 (17.6 Å – 1.20 Å) with a 0.04 °2 θ angular step and 40 seconds counting time per step, using a
97 D5000 diffractometer equipped with a SolX solid-state detector from Baltic Scientific
98 Instruments and $\text{CuK}\alpha$ radiation. Simulations were performed successively on the high- (30-
99 80 °2 θ $\text{CuK}\alpha$) and low-angle (5-30 °2 θ $\text{CuK}\alpha$) regions of the diffractograms. The high-angle
100 region is dominated by the scattering from two-dimensional hk bands, hkl reflections being
101 unresolved owing to the random layer stacking (random rotations and/or translations in the a -
102 b plane are systematic between adjacent layers). The in-plane unit-cell parameters (a and b)
103 were determined from the position of the band at ~1.41 Å (31,02 band using a C-centered
104 unit-cell, in which a and b axes are orthogonal), which is little affected by other structural
105 parameters. The unit-cell parameters relative to the layer stacking (c parameter, and α and β
106 angles) and the space group were not determined because of the turbostratic stacking which
107 leads to the lack of any 3D periodicity. Despite the intrinsic structural disorder, atomic
108 coordinates and site occupancies for layer (Mn) and interlayer (Na, Ni, Mn) cations were

109 however obtained from the simulation of the 11,20 band (at ~ 2.42 Å), because its profile is
110 strongly modulated by the crystal structure factor (Villalobos *et al.*, 2006; Drits *et al.*, 2007;
111 Lanson *et al.*, 2008). The size of the coherent scattering domains (CSDs), which are supposed
112 to have a disk-like shape in the *a-b* plane, also was derived from the modelling of the 11,20
113 band profile. The low-angle region, which contains 00*l* reflections, was used to verify the
114 lamellar character of the samples and to calculate the size of the CSDs along the c^* direction
115 (i.e. the mean number of layers stacked coherently) and the *d*(001) basal distance. Atomic
116 positions and occupancies were constrained to be identical for the simulation of the two sets
117 of reflections.

118 The background was supposed to decrease linearly over the two angular ranges. The
119 quality of fit was evaluated with the R_{wp} and GoF (Goodness of fit = R_{wp}^2/R_{exp}^2) parameters
120 (Attfield *et al.*, 1988; Howard and Preston, 1989). The uncertainty on the different structure
121 parameters could not be determined quantitatively because the trial-and-error approach,
122 required by the turbostratic nature of the samples investigated, does not allow the calculation
123 of a covariance matrix. However, the uncertainty on interlayer cation site occupancy can be
124 estimated to $\pm 1\%$ from the comparison of experimental and calculated XRD patterns
125 (Manceau *et al.*, 1997). Further qualitative assessment of uncertainties is provided by
126 Villalobos *et al.* (2006) and Lanson *et al.* (2008) using sensitivity tests.

128 **Results**

129 *Qualitative description of XRD profiles*

130 The diffractograms of Ni-sorbed δ -MnO₂ are typical of turbostratic birnessite-like crystals
131 (Fig. 1 – Drits *et al.*, 1997; Villalobos *et al.*, 2006). The peaks at ~ 7.6 Å and ~ 3.7 Å
132 correspond to basal reflections 001 and 002, although they do not form a strictly rational
133 series (Lanson *et al.*, 2008). The broad and asymmetric scattering maxima at ~ 2.42 Å,

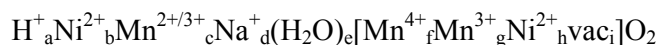
~1.41 Å and ~1.22 Å are indexed as 11,20, 31,02 and 22,40 bands, respectively, using a C-centred unit cell (Drits *et al.*, 1997, 2007; Webb *et al.*, 2005; Villalobos *et al.*, 2006; Lanson *et al.*, 2008). For all samples, the *d*-spacings of the 11,20 and 31,02 bands are in a ratio (~1.72) close to $\sqrt{3}$, indicative of a hexagonal layer symmetry. The symmetry of the 31,02 band profile also supports a layer unit cell that is hexagonal. If the layer unit cell were orthogonal this band would split into separate 31 and 02 bands and appear asymmetric (Drits *et al.*, 2007; Lanson *et al.*, 2008).

At first glance, all XRD patterns look similar, with the systematic presence of poorly defined 00*l* reflections in the low-angle region, and of *hk* bands exhibiting similar relative intensities in the high-angle one. Upon closer examination, it appears however that only NidBi2-4 and NidBi11-4, and NidBi2-7 and NidBi11-7, are statistically indistinguishable (Fig. 1). Therefore, in the following NidBi11-4 and NidBi11-7 are omitted. The 00*l* reflections are more intense at pH 7 than pH 4, and decrease with increasing Ni content for the pH 4 series. The broad hump at 50-55 °2θ becomes more pronounced as the Ni content increases in the two pH series (Fig. 1).

As shown by Drits *et al.* (2007), the modulations of the 11,20 band can be interpreted in structural terms. Specifically, XRD data resemble computations performed assuming hexagonal layer symmetry and ~17% vacant layer sites capped by interlayer Mn^{2+/3+} in triple-corner sharing position (TC linkage, Fig. 2 – Manceau *et al.*, 2002). The above described “hump” is indeed characteristic of a high number (>10%) of layer vacancies capped by “heavy” cations (Figs. 13a, b in Drits *et al.*, 2007). Furthermore, “heavy” interlayer cations are located mainly in TC rather than TE (triple edge sharing – Fig. 2) position (see Fig. 13c in Drits *et al.*, 2007). We can thus hypothesize as a starting model, that all Ni-sorbed δ-MnO₂ samples are turbostratic phyllomanganates, whose layers have a hexagonal symmetry and

bear significant amount of vacancies (>10%) capped mainly by “heavy” interlayer species (Mn or Ni) in TC or DC sites.

Combining this tentative structure model and the chemical data reported in Table 1, the following generic structural formula can be proposed:



where species between square brackets are located within the octahedral layer (vac stands for vacant layer sites) and those to the left of the brackets are interlayer species. The number of adjustable variables can be substantially reduced by physical and chemical constraints. First, EXAFS showed that Ni is predominantly located at TC and DC sites at pH 4 and pH 7 and $\text{Ni/Mn} > 1\%$ (Manceau *et al.*, 2007b – $\langle d(\text{Ni-O}) \rangle \sim 2.05 \pm 0.02 \text{ \AA}$). At lower Ni concentration, Ni partly fills vacant layer sites (E sites) in proportions which depend on the pH. This fraction was ignored in XRD simulations ($h = 0$) because it is minor (< 1%) compared to the number of Mn atoms in the manganese layers, and because Mn and Ni have similar scattering factors. Interlayer Mn cations are octahedrally coordinated as consistently reported in similar structures (Chukhrov *et al.*, 1985; Silvester *et al.*, 1997; Villalobos *et al.*, 2006; Lanson *et al.*, 2008). In the simulations, sodium was coordinated to three water molecules as reported previously (Post and Veblen, 1990; Villalobos *et al.*, 2006). Finally, relative amounts of Mn^{4+} , Mn^{3+} , Ni^{2+} , and Na^+ were constrained to their chemical values (Table 1), and protons were eventually introduced to ensure the electro-neutrality of the structure. Parameters adjusted during the fitting process were thus limited to the distribution of Mn^{3+} cations between layer and interlayer sites, the position of interlayer Na^+ and coordinated H_2O molecules, and the coordinates of interlayer Mn, Ni, and associated H_2O molecules along the c^* axis.

182 *Simulation of the high-angle (30-80 °2θ Cu-Kα) region*

183 In a first attempt, atomic coordinates were assumed to be identical for all samples, as the
184 synthesis and sorption procedures were analogous, and only site occupancies were adjusted,
185 together with unit-cell parameters and CSD sizes. Once the main features of all XRD patterns
186 were satisfactorily reproduced, atomic coordinates were adjusted for each sample, but the fit
187 to the data could not be improved significantly. Atomic positions are thus identical for all
188 samples which differ only by their respective unit-cell parameters, CSD sizes, and their
189 contents of the various interlayer species (Tables 2, 3). The best fits to the XRD data are
190 shown in Figure 3. The plausibility of the proposed models was assessed by calculating the
191 valence of all atoms in the structure (Table 4 – Brown, 1996), which is an efficient way to
192 constrain the model (Gaillot *et al.*, 2003).

193 The crystals are systematically nanosized (50-56 Å in diameter in the layer plane).
194 Layers contain a significant amount (16-18.5%) of vacant sites, which are capped on one or
195 the two sides by octahedrally coordinated Mn³⁺ and/or Ni²⁺, depending on the Ni/Mn loading
196 and on the equilibration pH. Na⁺ and H⁺ compensate for the remainder of the negative layer
197 charge. With increasing Ni loading, the number of Ni complexes increases at the expense of
198 Na⁺ and/or interlayer Mn, depending on the pH series. At pH 4, Ni preferentially replaces
199 Na⁺, the number of ⁵⁵Mn remaining constant within error, whereas Ni replaces both Na⁺,
200 ⁵⁵Mn, and ⁵⁴Mn at pH 7.

201 Interlayer Mn³⁺ and Ni²⁺ are octahedrally coordinated and located either above/below
202 vacant layer sites or in TE sites. Sodium is located in the interlayer mid-plane coordinated to
203 three water molecules at 2.30 Å, 2.89 Å and 2.95 Å (Fig. 4). The first distance is shorter than
204 commonly observed (i.e. ~2.45 Å – Angeli *et al.*, 2000) but has already been reported in the
205 literature (Brown, 1977). The prevalence of monolayers precludes oxygen atoms from
206 adjacent layers to provide bond valence to Na, and thus favours strong interactions with

interlayer H₂O molecules. The first coordination sphere of Na⁺ is limited to ~3.0 Å, consistent with theoretical studies (Delville, 1992). However, the sum of bond valence with H₂O molecules (O6) and layer oxygen (O1) is not sufficient to fully compensate the Na⁺ charge (Table 4), as discussed in the following section. The position of H₂O molecules coordinated to interlayer Na⁺ allows for the formation of strong H-bonds with layer oxygen atoms (O_{layer}), with $d(\text{H}_2\text{O}-\text{O}_{\text{layer}}) = 2.71 \text{ \AA}$.

To match the measured mean oxidation degree of Mn, Mn³⁺ cations have to be included in the octahedral layers, but the number of ^EMn³⁺ remains limited, peaking at ~9% of layer octahedra for sample NidBi2-4 (Table 1). This low number is consistent with the hexagonal symmetry of the layer (Gaillot *et al.*, 2005, 2007; Manceau *et al.*, 2005). The in-plane *b* unit-cell parameter ($2.835 \text{ \AA} \leq b \leq 2.840 \text{ \AA}$) are similar to those reported previously for δ-MnO₂ (2.838 \AA – Villalobos *et al.*, 2006). The sensitivity to this parameter was assessed with sample NidBi105-4 from the variation of R_{wp} as a function of the *b* parameter ($a = \sqrt{3} \times b$ – Fig. 5). The estimated error on *b* is ±0.001 Å.

Simulation of the low-angle (5-30 °2θ) region

The position, amplitude, and width of the two 00*l* reflections present over this low-angle region were simulated using the optimal structure models and adjusting only the out-of-plane *d*(001) parameter and CSD size along the *c*^{*} direction. Experimental data were fitted with mean CSD sizes of $9.5/7.3 = 1.3$ to $15.3/7.3 = 2.1$ layers (Table 2, Fig. 6). Thus, most crystals consist of isolated layers. When a diffracting crystallite contains two or more layers, its layer stacking is random (i.e., turbostratic) as no significant modulations are visible on *hk* bands (see Lanson *et al.*, 2008, for a discussion). The *d*(001) basal distance determined (7.3 Å) is slightly higher than usually reported for both ordered and disordered birnessites (7.2 Å). This

increased basal distance is consistent with the weak bonding between adjacent layers supported by the small CSD sizes.

Discussion

Composition of the interlayer

Except for Na, all atomic positions are consistent with those previously determined for metal-sorbed birnessite-like compounds, either well or poorly crystallised (Manceau *et al.*, 1997, 2002; Lanson *et al.*, 2002b, 2008; Villalobos *et al.*, 2006). The Na⁺ position [(-0.525, 0, 1/2) and equivalent positions] however provides this cation with an environment similar to that commonly reported in Na-bearing disordered birnessite (Villalobos *et al.*, 2006; Lanson *et al.*, 2008) with $d(\text{Na}-\text{O}_{\text{layer}}) \sim 2.66 \text{ \AA}$. Na⁺ coordination consists essentially of adjacent O_{layer} atoms and interlayer H₂O molecules, however failing to fully compensate the charge of this cation (Table 4). The nanocrystalline character of $\delta\text{-MnO}_2$, and specifically the prevalence of monolayers, may account for the compensation of the remaining charge, as H₂O molecules hydrating the crystals may actually contribute to charge compensation. For crystals composed of more than one layer, O_{layer} from adjacent layers could also contribute to compensate the charge of interlayer Na, but sample turbostratism precludes the calculation of this bond valence.

The sensitivity of XRD patterns calculated for turbostratic birnessite to small variations of the site coordinates or occupancies has been discussed previously (Villalobos *et al.*, 2006; Drits *et al.*, 2007; Lanson *et al.*, 2008), and is not discussed further here to assess model robustness. The proposed structure model implies the replacement of interlayer Mn and Na cations by interlayer Ni (Table 3) with increasing Ni/Mn content. If based on XRD data only, this model could appear questionable as XRD is sensitive only to the distribution of electronic density but does not provide element-specific information. One could thus argue that XRD

simulation demonstrates essentially an increase of the electronic density above/below vacant layer sites with increasing Ni/Mn content, especially for the pH 7 series. This modification of the electron density distribution could possibly result from a limited adsorption of Ni assuming a constant number of interlayer Mn. Various constraints allow rejection of this alternative structure model. First, the two elements do not have the same *z*-coordinates, thus allowing their differentiation in the interlayer. Second, the mean oxidation degree of Mn increases with increasing Ni loading, showing that the number of Mn³⁺, which is dominantly present as an interlayer species, decreases with increasing Ni/Mn content. In addition, a Ni²⁺-for-Na⁺ exchange would lead to a strong excess of charge in δ -MnO₂ structure, whereas the Ni²⁺-for-Mn³⁺ exchange avoids this effect despite the increased number of interlayer cations above/below vacant layer sites. Finally, the evolution of the Ni/Mn ratio requires increasing the Ni content in the XRD simulations. EXAFS showed that Ni was not present as a precipitate (Manceau *et al.*, 2007b), that would most likely have been detected also by XRD. The hypothesis of Ni sorption on the edges of δ -MnO₂ crystals at a octahedral layer site (E site – Fig. 2) may also be rejected as it would lead to a significant increase of the CSD size of these crystals within the *a-b* plane. The sorption of 2 Ni octahedra on the edges of δ -MnO₂ crystals would increase indeed the CSD size by 20-25% (from 54 to 66 Å in diameter), which would be easily detected by XRD owing to the high sensitivity of calculated patterns to this parameter (Villalobos *et al.*, 2006). For sample NidBi105-4, such an increase of the CSD size would lead to R_{wp} and GoF values of 7.04% and 6.62, respectively, about two times the value of the optimal model (5.00%, and 3.33, respectively – Fig. 3). Such sorption would impact also the EXAFS signal, inconsistent with the data since edge-sharing Ni-Mn pairs are excluded at high Ni/Mn (Manceau *et al.*, 2007b).

The local environment of Ni can be constrained further from Ni-EXAFS results obtained on the same samples by Manceau *et al.* (2007b). According to these results, Ni sorbs

predominantly as ^{TC}Ni and ^{DC}Ni complex at pH 4-7 and Ni/Mn ratios > 1%. The XRD and EXAFS models are therefore consistent as the ^{TC}Ni and ^{DC}Ni sites are equivalent for XRD, the investigated solids being too disordered to allow the discrimination of small differences in atomic coordinates. Despite the partial sorption of Ni at DC sites, that is on particle edges (Manceau *et al.*, 2007b), no increase of the CSD is observed. This observation is possibly due to the multiplicity of Ni sorption sites (E, TC, DC) and to the possibility for Ni atoms to sorb on the two DC sites apart the same edge octahedron. Our results also agree with those reported by Peacock and Sherman (2007b) in their study of Ni sorption on synthetic hexagonal birnessite, a well crystallised phyllomanganate in which one sixth of the layer sites are vacant and capped by interlayer Mn^{3+} (Drits *et al.*, 1997; Silvester *et al.*, 1997; Lanson *et al.*, 2000). At pH 7, Peacock and Sherman (2007b) observed that ~90% of total Ni occupy TC sites. The apparent absence of ^{DC}Ni in their study is likely related to the larger lateral dimension of birnessite layers relative to δ - MnO_2 as the proportion of border sites, and thus surface reactivity of phyllomanganates in general, tremendously decreases when layer size increases (Tournassat *et al.*, 2002; Villalobos *et al.*, 2005; Webb *et al.*, 2005).

Sorption of metal cations in TE site has been seldom described (Lanson *et al.*, 2002b, 2008). Here, it may be favoured by the combined effects of the high density of interlayer cations in TC position and the probable presence of some layer Mn^{3+} cations (Table 1). The occupancy of the two TC positions apart the same vacancy induces electrostatic repulsion, especially when Ni^{2+} is facing a Mn^{3+} cation, that can be minimised by moving one cation in TE position. In addition, the combined presence of Mn^{3+} cations and of vacant sites in the octahedral layers results in the strong undersaturation of some O_{layer} atoms that is best compensated for by the presence of interlayer cations in both TC and TE sites (Lanson *et al.*, 2002b).

Ni sorption mechanism

Although similar structure models were obtained for the two δ -MnO₂ series, the mechanism of Ni sorption likely differs at the two pHs, as attested macroscopically by the twofold increase in the evolution of the Mn mean oxidation degree with Ni loading at pH 7 (Fig. 7). Chemical data and XRD simulations suggest that at pH 4 Ni²⁺ replaces preferentially Na⁺ and H⁺, Mn³⁺ being strongly bound to the octahedral layers, whereas Ni²⁺ more readily exchanges for Mn³⁺ at pH 7. This contrasting behaviour could result from the higher number of Mn³⁺ cations in the octahedral layers at low pH. As discussed above, the coexistence in octahedral layers of vacant layer sites and Mn³⁺ cations induces a strong undersaturation of O_{layer} atoms, and therefore favours the binding of high-charge interlayer cations such as Mn³⁺.

Comparison to structure models previously reported for δ -MnO₂

For a long time, the structure of δ -MnO₂ has been controversial. This compound, now known to be analogous to vernadite and turbostratic birnessite, was first reported by McMurdie (1944), and described as poorly crystalline cryptomelane (McMurdie and Golovato, 1948). In contrast, Feitknecht and Marti (1945) suggested a lamellar structure similar to pyrochroïte. The structural analogy between δ -MnO₂ and birnessite was suggested by Giovanoli (1969, 1980), and a structure model was proposed recently by Villalobos *et al.* (2006) using XRD and EXAFS spectroscopy. Despite the availability of structure models, and the demonstrated potential for structure characterization (Drits *et al.*, 2007), δ -MnO₂ is however commonly referred to as “amorphous manganese oxide” or as “hydrous manganese oxide – HMO” (Xu and Yang, 2003; Boonfueng *et al.*, 2005; Huang *et al.*, 2007) without precision on important structural parameters such as the origin of the layer charge (vacant layer sites vs Mn³⁺ in the layers).

The structure model proposed here differs in three points from the model proposed by Villalobos *et al.* (2006), for another sample synthesized following the same protocol. Previously, the structure was considered to contain only Mn^{4+} , because the average oxidation degree obtained by the oxalate and iodine titration methods was 4.02 ± 0.02 (see Villalobos *et al.*, 2003, for details). Here, a value of 3.80 ± 0.03 has been measured at pH 7 and low Ni content (NidBi2-7), suggesting the presence of Mn^{3+} or Mn^{2+} . The presence of Mn^{3+} both within the octahedral layer and as interlayer species at TC and TE sites is supported by chemical, bond valence, and XRD results which consistently show that Mn^{2+} occurs only as a minor interlayer species if present at all. In particular, the presence of Mn^{2+} at TC or TE sites is not consistent with the coordination of interlayer Mn cations determined from XRD modelling requiring the mean Mn-O bond length to be $\sim 0.15 \text{ \AA}$ longer than in the proposed structure model (Table 2). Although $\delta\text{-MnO}_2$ was equilibrated at pH 8 in the previous study, the 0.2 difference in Mn mean oxidation state is likely experimental because the oxalate and iodine methods used previously are less accurate than the Mohr salt / sodium pyrophosphate method used here (Gaillot, 2002). This hypothesis was verified by re-measuring the original $\delta\text{-MnO}_2$ sample (pH 8) studied by Villalobos *et al.* (2006) with the second titration method. A new value of 3.88 ± 0.03 was obtained, consistent with the 3.80 ± 0.03 value measured for NidBi2-7 taking into account the decrease in mean oxidation degree of manganese with decreasing pH observed here and for soil manganese oxides (Negra *et al.*, 2005). Note also that the new model yielded a better fit to XRD data ($R_{\text{wp}} = 6.2\%$ – GoF ~ 4.6) than the previous model ($R_{\text{wp}} = 10.7\%$ – GoF ~ 9.4). The second difference, which derives directly from the lower mean oxidation degree of Mn, is the presence of Mn^{3+} in the interlayer. Multivalent cations in TC and TE sites are more efficient at compensating the charge deficit of most undersaturated O_{layer} atoms than Na^+ and H^+ only, as in the previous model. The presence of multivalent cations at TC positions is also consistent with other structural studies

on δ -MnO₂ and vernadite (Manceau *et al.*, 2007b; Peacock and Sherman, 2007b; Lanson *et al.*, 2008). Third, the new model has 18% vacant layer sites, compared to 6% for the δ -MnO₂ sample studied previously. However, the new value does not reflect the actual number of vacant sites in the layer when CSDs are small in the *a-b* plane (Webb *et al.*, 2005). Here, with a CSD size of ~ 55 Å, compared to ~ 120 Å previously, a large fraction of Ni atoms is sorbed on border sites as ^{DC}Ni complex when Ni/Mn > 1% (Fig. 2 – Manceau *et al.*, 2007b). This complex increases the apparent number of layer vacancies seen by XRD because it has 2-3 nearest Mn neighbours instead of 6 for ^{TC}Ni on basal planes. Thus, the δ -MnO₂ crystals studied here have fewer layer vacancies than determined by XRD, because some of them are actually border sites. The distinction between interlayer and border sites becomes flimsy when crystals are vanishingly small.

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538

Figure captions

FIG. 1. XRD patterns of Ni-sorbed δ -MnO₂. **(a)** pH 4. **(b)** pH 7. The grey bar indicates a 5 \times scale factor for the high-angle region except for samples NidBi56-7 and NidBi177-7 (1.67 \times scale factor). For each pH series, the sample with the lowest Ni/Mn ratio is systematically shown as a light grey line to emphasize the modification of XRD traces with Ni content (arrows).

FIG. 2. Schematic representation of layer and interlayer sites reported in the literature for metal cations (including Mn) in δ -MnO₂. TC, DC and TE labels refer respectively to triple-corner sharing, double-corner sharing and triple-edge sharing sites. E label refers to layer sites.

FIG. 3. Simulations of the 11,20, 31,02 and 22,40 X-ray scattering bands (C-centred layer cell) for Ni-sorbed δ -MnO₂ samples. Black crosses are experimental data, solid grey overplots are calculated profiles, and solid lines at the bottom are difference plots. Structural parameters used for the simulations are listed in Tables 2, and 3.

FIG. 4. Structure model of Ni-sorbed δ -MnO₂. **(a)** Projection on the a - b plane. **(b)** Projection on the b - c^* plane. Shaded octahedra represent layer Mn and its coordination sphere. Bonds between interlayer species and coordinating oxygens are shown in ball-and-stick. The coordinates of the different species along the c^* axis are given in Å.

FIG. 5. Simulations of the 31,02 X-ray scattering band (C-centred layer cell) for sample NidBi105-4. Gray crosses are experimental data, and lines are calculated profiles. The

optimum fit to the data (solid line) was obtained with $b = 2.835 \text{ \AA}$ and $a = \sqrt{3} \times b$ (Table 2). Varying b by $\pm 0.01 \text{ \AA}$ with $a = \sqrt{3} \times b$ significantly decreases the fit quality. The inset shows the evolution of R_{wp} with b .

FIG. 6. Simulations of the 001 and 002 diffraction lines for Ni-sorbed δ - MnO_2 . Patterns as in Figure 4. Structural parameters used for the simulations are listed in Tables 2 and 3.

FIG. 7. Average oxidation degree of Mn as a function of Ni/Mn ratio for Ni-sorbed δ - MnO_2 samples (circles: pH 4, triangles: pH 7).

TABLE 1. Chemical composition of Ni-sorbed δ -MnO₂ expressed as atomic ratios.

Sample	Na/Mn (%)	Ni/Mn (%)	Mn Ox.	Layer Mn ³⁺
NidBi2-4	18.39 \pm 0.30	0.23 \pm 0.23	3.74 \pm 0.03	0.09
NidBi11-4	16.99 \pm 0.27	1.07 \pm 0.23	3.73 \pm 0.03	N.D.
NidBi50-4	10.90 \pm 0.05	4.97 \pm 0.04	3.75 \pm 0.02	0.08
NidBi105-4	5.57 \pm 0.15	10.57 \pm 0.15	3.77 \pm 0.02	0.07
NidBi2-7	26.53 \pm 0.19	0.25 \pm 0.14	3.80 \pm 0.03	0.04
NidBi11-7	26.80 \pm 0.40	1.07 \pm 0.24	3.80 \pm 0.03	N.D.
NidBi56-7	20.87 \pm 0.22	5.66 \pm 0.15	3.85 \pm 0.02	0.01
NidBi177-7	7.61 \pm 0.22	17.78 \pm 0.21	3.94 \pm 0.01	0.00

Note: Mn Ox. stands for “oxidation degree”. Layer Mn³⁺ is calculated from the average oxidation degree of Mn and from the number of interlayer Mn atoms (Table 3), which are considered to be trivalent. Uncertainties on the mean values are calculated as the mean of standard errors (Webster, 2001). Sample names as in Manceau *et al.* (2007b)

TABLE 2. Crystal data for Ni-sorbed δ -MnO₂.

	NidBi2-4	NidBi50-4	NidBi105-4	NidBi2-7	NidBi56-7	NidBi177-7
a (Å)	4.916	4.912	4.910	4.917	4.919	4.917
b (Å)	2.838	2.836	2.835	2.839	2.840	2.839
$d(001)$ (Å)	7.3	7.3	7.3	7.3	7.3	7.3
Average CSD along c (Å)	11.0	10.2	9.5	12.4	15.3	11.0
CSD in the a - b plane (Å) ^a	56	54	54	54	54	50
R_{wp} (%) ^b	5.72-6.32	4.12-5.17	4.97-5.00	8.74-6.15	5.22-5.82	5.21-6.06
GoF (%) ^b	6.49-4.53	3.57-3.32	5.41-3.33	15.40-4.45	8.42-6.52	5.41-4.17

^a Diameter of the disk-like coherent scattering domains. ^b First and second values are calculated over the low- and high-angle regions, respectively.

TABLE 3. Structural parameters of Ni-sorbed δ -MnO₂ derived from XRD.

Atom	x^a	y	z	ζ^b	Occ. ^c NidBi2-4	Occ. ^c NidBi50-4	Occ. ^c NidBi105-4	Occ. ^c NidBi2-7	Occ. ^c NidBi56-7	Occ. ^c NidBi177-7
Mn _{layer} (Mn1)	0.000	0.000	0.000	0.000	0.82	0.82	0.82	0.82	0.815	0.84
O _{Mn1} (O1)	0.333	0.000	0.139	1.015	2.00	2.00	2.00	2.00	2.00	2.00
^{TC} Mn (Mn2)	0.000	0.000	0.299	2.183	0.14	0.16	0.16	0.10	0.085	0.07
H ₂ O _{Mn2} (O2)	-0.333	0.000	0.472	3.446	0.42	0.48	0.48	0.30	0.255	0.21
^{TE} Mn (Mn3)	-0.333	0.000	0.299	2.183	0.03	0.00	0.00	0.05	0.04	0.00
H ₂ O _{Mn3} (O3)	0.000	0.000	0.472	3.446	0.09	0.00	0.00	0.15	0.12	0.00
^{TC} Ni (Ni1)	0.000	0.000	0.306	2.234	0.00	0.04	0.07	0.00	0.05	0.13
H ₂ O _{Ni1} (O4)	-0.333	0.000	0.486	3.548	0.00	0.12	0.21	0.00	0.15	0.39
^{TE} Ni (Ni2)	-0.333	0.000	0.315	2.300	0.00	0.02	0.02	0.00	0.00	0.02
H ₂ O _{Ni2} (O5)	0.000	0.000	0.486	3.548	0.00	0.06	0.06	0.00	0.00	0.06
Na _{interlayer} (Na) ^d	-0.525	0.000	0.500	3.650	0.18	0.06	0.06	0.24	0.18	0.06
H ₂ O _{Na+} (O6) ^e	0.200	0.000	0.500	3.650	0.54	0.18	0.18	0.72	0.54	0.18

^a Atomic coordinates x , y , z are expressed as fractions of the a , b and $d(001)$ parameters, respectively. Positions are given in the $(x, 0, z)$ form. Equivalent positions are $(x + \frac{1}{2}, \frac{1}{2}, z)$, because the unit cell is C-centred. Additional equivalent positions are $(-x, 0, -z)$. ^b Coordinates along the c^* axis, ζ , are expressed in Å to emphasize the thickness of layer and interlayer polyhedra. ^c Occupancies are given per half

formula unit as the sum of the occupancies for all equivalent positions. ^d Additional symmetry operations: $(-x/2 - 1/2, 3x/2 + 1/2, z)$, and $(-x/2 - 1/2, -3x/2 - 1/2, z)$. ^e Additional symmetry operations: $(-x/2, 3x/2, z)$, and $(-x/2, -3x/2, z)$.

Unrefined Debye-Waller thermal factors (B) are equal to 0.5 for Mn_{layer}, 1.0 for O_{layer}, interlayer Mn and Ni, 1.5 for H₂O molecules bound to interlayer Mn and Ni, and 2.0 for other interlayer species (alkali cations and H₂O molecules).

TABLE 4. Bond valences calculated^a for Ni-sorbed δ -MnO₂

	O1 ^b	O1 ^c	O1 ^d	O1 ^e	O2/O3	O4/O5	O6	Σ	Formal valence
Mn1	0.625 $\times 6 \rightarrow$ $\times 3 \downarrow$	0.625 $\times 2 \downarrow$	0.625 $\times 2 \downarrow$	0.625 $\times 2 \downarrow$				3.75	4
Mn2, Mn3		0.509 $\times 3 \rightarrow$			0.433 $\times 3 \rightarrow$			2.8	3
Ni1, Ni2			0.298-0.352 ^f $\times 3 \rightarrow$			0.300-0.317 ^f $\times 3 \rightarrow$		1.9	2
Na ⁺				0.091 0.012 $\times 2 \rightarrow$			0.261, 0.053, 0.045 ^g	0.5	1
H ⁺				0.105 ^h	0.815 $\times 2 \downarrow$	0.815 $\times 2 \downarrow$	0.815 $\times 2 \downarrow$		
Σ	1.9	1.8	1.5-1.6 ^f	1.3-1.4 ⁱ	2.1	1.9	1.7-1.9 ^g		

^a Bond valences in valence unit (v.u.) were calculated using the Valence for Dos program (v. 2.0 - http://www.ccp14.ac.uk/solution/bond_valence/index.html – Brown, 1996) and the parameters from Brese and O' Keeffe (1991). ^b O1 coordinated to 3 Mn⁴⁺ in Mn1 (Table 3). ^c O1 coordinated to 2 Mn⁴⁺ in Mn1 and 1 Mn³⁺ in Mn2 or Mn3 (Table 3). ^d O1 coordinated to 2 Mn⁴⁺ in Mn1 and 1 Ni²⁺ in Ni1 or Ni2 (Table 3). ^e O1 coordinated to 2 Mn⁴⁺ in Mn1 (Table 3). ^f Depending on whether Ni is located in Ni1 or in Ni2. ^g Na⁺ is coordinated to 3 H₂O molecules at 2.30, 2.89, and 2.95 Å. ^h O6-H-O1 H-bond. ⁱ Depending on whether this O1 receives additional valence from Na⁺ or from H⁺ through H-bond.

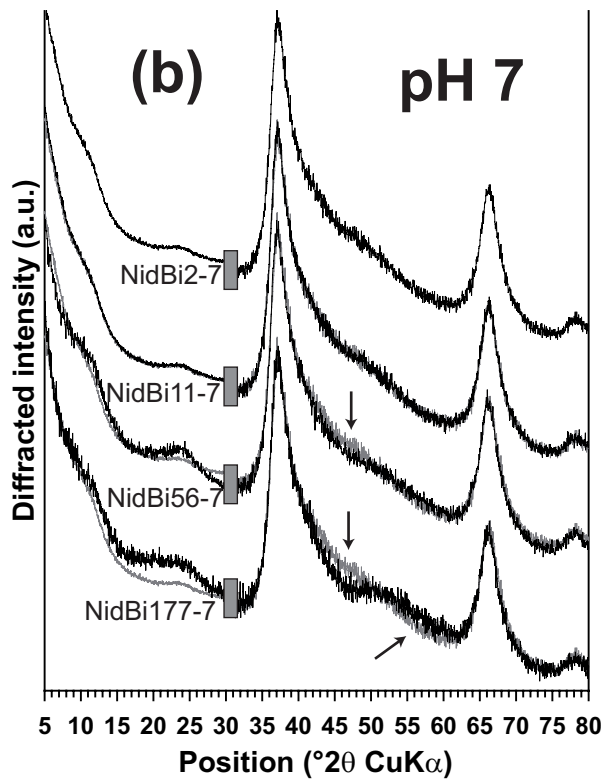
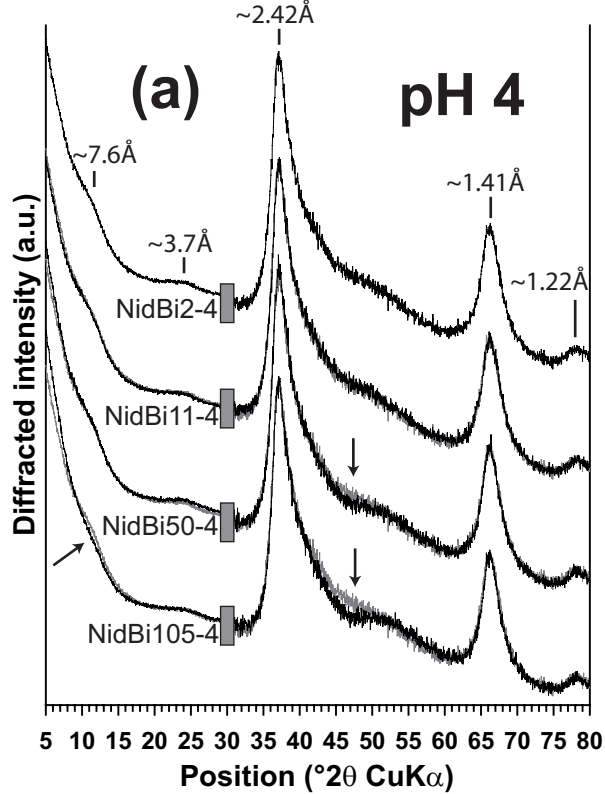


Figure 1

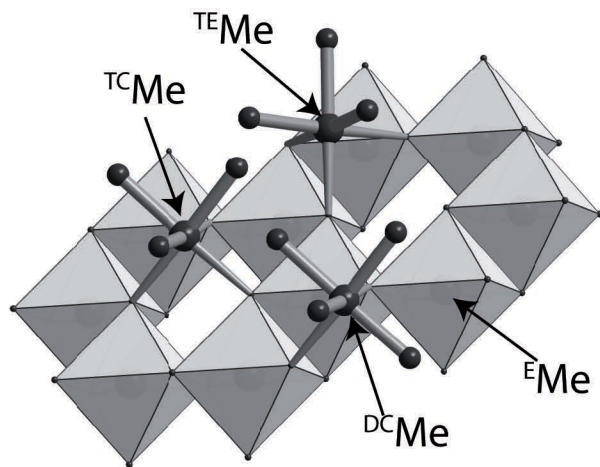


Figure 2

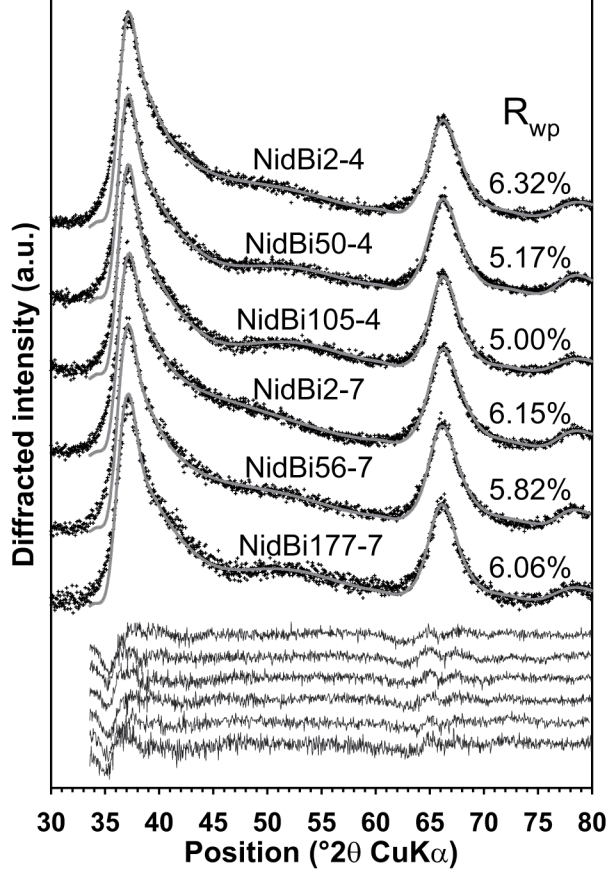


Figure 3

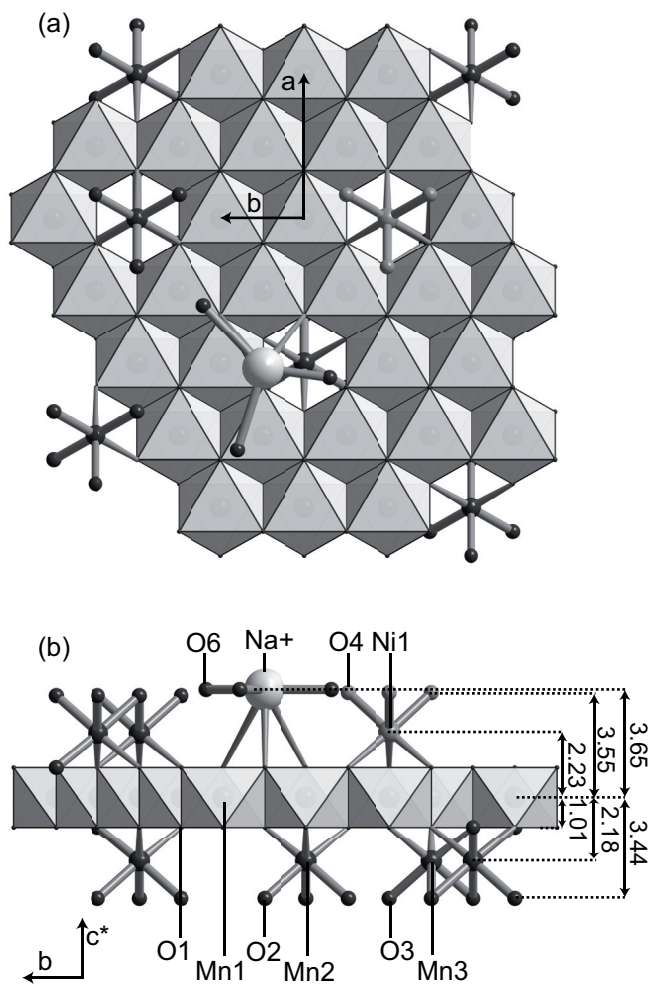


Figure 4

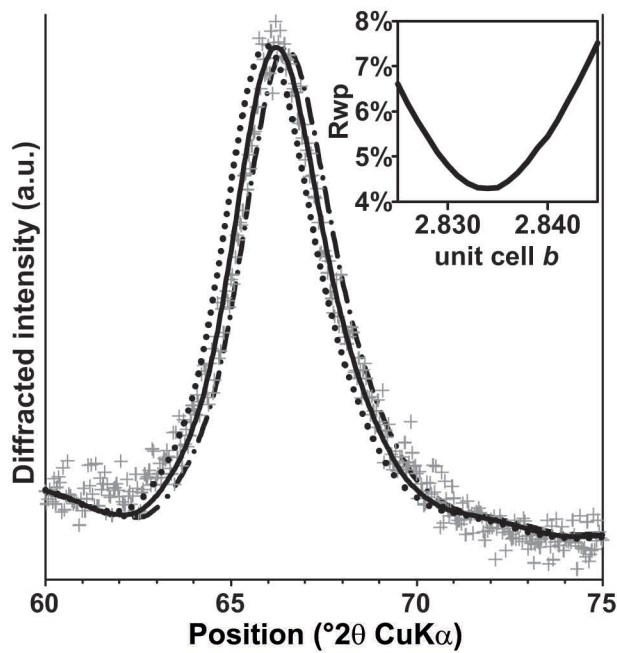


Figure 5

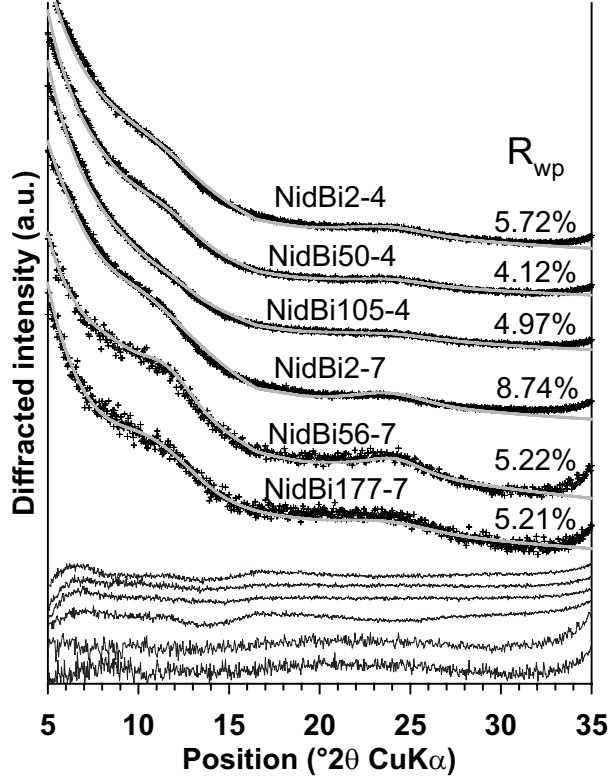


Figure 6

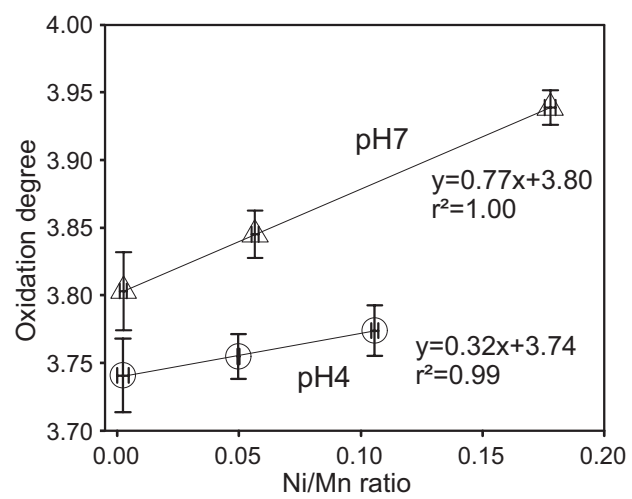


Figure 7